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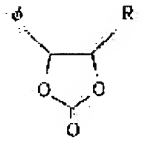
(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To control decomposition of an electrolyte to the minimum to provide a nonaqueous electrolyte secondary battery of high energy density excellent in a cycle characteristic.
SOLUTION: In a nonaqueous electrolyte secondary battery provided with a negative electrode and a positive electrode containing carbonacous material capable of storing and releasing lithium, a nonaqueous electrolyte comprising a solute and an organic solvent, and a separator, the organic solvent contains at least one kind selected from the group of compounds expressed by formula I or formula II, where ϕ represents a phenyl group substituted with alkyl groups or not substituted, R represents hydrogen atom, a 1-4C alkyl group or a phenyl group substituted or not substituted with alkyl groups.



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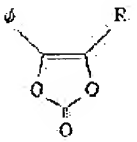

II

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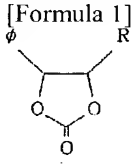
3.In the drawings, any words are not translated.

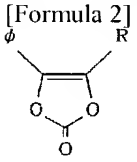
CLAIMS

[Claim(s)]
[Claim 1] The nonaqueous electolyte rechargeable battery characterized by the thing for which said organic system solvent is chosen from the compound expressed with the compound or the following general formula (II) expressed with the following general formula (I) in the nonaqueous electolyte rechargeable battery equipped with the nonaqueous electolyte which consists a lithium of the negative electrode and positive electrode containing occlusion and the carbonaceous ingredient which can be emitted, and a solute and an organic system solvent, and the separator, and which contain a kind at least.
[Formula 1]



(I)

(phi expresses among a formula the phenyl group which may have the alkyl group, and R expresses the phenyl group which may have the hydrogen atom, the carbon number 1, the alkyl group of 4, or the alkyl group)
[Formula 2]



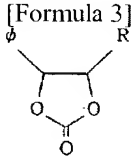
(II)

(The inside of a formula, and phi and R are synonymous with a formula (I))
[Claim 2] The nonaqueous electolyte rechargeable battery according to claim 1 characterized by an organic system solvent containing annular carbonate or chain-like carbonate further.
[Claim 3] The nonaqueous electolyte rechargeable battery according to claim 1 or 2 characterized by a solute being lithium salt.
[Claim 4] The nonaqueous electolyte rechargeable battery according to claim 1 to 3 characterized by the sum total content of the compound of the formula in an organic system solvent (I) and a formula (II) being 0.05 - 40 % of the weight.
[Claim 5] The nonaqueous electolyte rechargeable battery according to claim 1 to 4 with which solute concentration in a nonaqueous electolyte is characterized by being 0.5-2 mols/l.

[Translation done.]

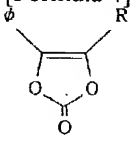
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to a nonaqueous electolyte rechargeable battery. In detail, it is related with the nonaqueous electolyte rechargeable battery using the electrolytic solution containing specific aromatic series carbonate. Since the cycle property is excellent while suppressing disassembly of the electrolytic solution to the minimum and obtaining a high capacity, the cell of this invention can attain miniaturization of a nonaqueous electolyte rechargeable battery, and high performance-ization.
[0002]
[Description of the Prior Art] A lithium secondary battery with a high energy density attracts attention with lightweight-izing of an electric product in recent years, and a miniaturization, and various researches are done. Moreover, the improvement of a cell property is also demanded with expansion of Field of application of a lithium secondary battery. As a solvent of the electrolytic solution of such a lithium secondary battery, the nonaqueous organic solvent of carbonate, such as ethylene carbonate, propylene carbonate, diethyl carbonate, and gamma-butyrolactone, or ester has been used, for example.
[0003]
[Problem(s) to be Solved by the Invention] However, about a lithium secondary battery, there was operating potential width of face more than 3V, and even if it used the electrolytic solution which contains the above comparatively stable nonaqueous organic solvents by using a lithium with very high activity, in the charge-and-discharge process, disassembly of the electrolytic solution in an electrode surface was not avoided, but originated in it, and had problems, such as decline in charge-and-discharge effectiveness, and a fall of a cycle property. This invention is made in order to solve this trouble, it suppresses disassembly of the electrolytic solution of a nonaqueous electolyte rechargeable battery to the minimum, and offers the nonaqueous electolyte rechargeable battery of the high energy consistency which was excellent in the cycle property.
[0004]
[Means for Solving the Problem] this invention persons came to complete a header and this invention for the ability of the nonaqueous electolyte rechargeable battery using the electrolytic solution containing specific aromatic series carbonate to solve said technical problem, as a result of inquiring wholeheartedly in view of this situation. The summary of this invention is a nonaqueous electolyte rechargeable battery characterized by the thing for which said organic system solvent is chosen from the compound expressed with the compound or the following general formula (II) expressed with the following general formula (I) in the nonaqueous electolyte rechargeable battery equipped with the nonaqueous electolyte which consists a lithium of the negative electrode and positive electrode containing occlusion and the carbonaceous ingredient which can be emitted, and a solute and an organic system solvent, and the separator, and which contain a kind at least.
[0005]
[Formula 3]



(I)

[0006] (phi expresses among a formula the phenyl group which may have the alkyl group, and R expresses the phenyl group which may have the hydrogen atom, the carbon number 1, the alkyl group of 4, or the alkyl group)
[0007]
[Formula 4]



(II)

[0008] (The inside of a formula, and phi and R are synonymous with a formula (I))
[0009]
[Function] By using the organic system solvent containing the annular carbonate compound which has a phenyl group, the quite

stable protective coating of lithium ion permeability generates to the electrode surface which touches the electrolytic solution, and it is thought that disassembly of the electrolytic solution is controlled with this coat. And the rechargeable battery which was excellent in the cycle property is producible by controlling disassembly of the electrolytic solution.

[0010]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The rechargeable battery of this invention is characterized by the thing of the compound by which the organic system solvent of the nonaqueous electolyte is expressed with a formula (I) or a formula (II) for which a kind is contained at least.

[0011] In a formula (I) or a formula (II), phi expresses the phenyl group which may have the alkyl group. Here, although especially limitation is not carried out about the class and number of alkyl groups, as the example, a methyl group, an ethyl group, a propyl group, butyl, a hexyl group, etc. are mentioned, for example, and a methyl group and an ethyl group are especially desirable [a carbon number 1 thru/or the alkyl group of 8 are desirable, and] also in these.

[0012] And as an example of a phenyl group in which you may have the alkyl group, a phenyl group, a methylphenyl radical, an ethyl phenyl group, a propyl phenyl group, a buthylphenyl radical, a hexyl phenyl group, a dimethylphenyl radical, etc. are mentioned, for example.

[0013] Moreover, R expresses the phenyl group which may have the hydrogen atom, the carbon number 1, the alkyl group of 4, or the alkyl group. Here, a carbon number 1 thru/or the alkyl group of 4 express a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, i-butyl, sec-butyl, and tert-butyl. Moreover, the phenyl group which may have the alkyl group is similarly defined as phi, although it is what became independent, respectively.

[0014] And in the annular carbonate which has such a phenyl group, as an example of the compound of a formula (I), phenylethylene carbonate, diphenylethylene carbonate, methylphenyl ethylene carbonate, ethyl phenylethylene carbonate, etc. are mentioned, and phenyl vinylene carbonate, diphenyl vinylene carbonate, methylphenyl vinylene carbonate, ethyl phenyl vinylene carbonate, etc. can be mentioned as an example of the compound of a formula (II), for example. Two or more sorts may be mixed and these may be used.

[0015] in addition, about the compound of a formula (I) or a formula (II) a well-known approach -- for example, (Clark, J.R., J.Org.Chem., and 24 and 1088 (1959) --) 27 Morris, L.R., J.Org.Chem., 1451 (1962), Breitbeil, F.W., et al., Transactions, Ill.State Based on the approach of a publication, it is compoundable to Acad.Sci., 67,139 (1974), etc.

[0016] As organic system solvent components other than the annular carbonate which has a phenyl group, ethylene carbonate, Annular carbonate, such as propylene carbonate and butylene carbonate Chain-like carbonate, such as dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate Cyclic ester, such as gamma-butyrolactone and gamma-valerolactone, methyl acetate, Chain-like ester, such as methyl propionate, a tetrahydrofuran, 2-methyl tetrahydrofuran, Sulfur-containing organic solvents, such as chain-like ether, such as cyclic ether, such as tetrahydropyran, dimethoxyethane, and dimethoxymethane, sulfolane, and diethyl sulfone, etc. are mentioned. Two or more kinds may be mixed and these solvents may be used.

[0017] In addition, as for the compound of a formula (I) or a formula (II), the sum total content in an organic system solvent is usually used 0.05 to 40% of the weight so that it may become preferably 0.1 - 20% of the weight of within the limits. Since the viscosity of the electrolytic solution will become high, conductivity will become low and the engine performance of a cell will fall if sufficient coat formation is not made as the content is less than 0.05 % of the weight, and it exceeds 40 % of the weight, it is not desirable.

[0018] About a solute, lithium salt is usually used. Although especially limitation is not carried out about lithium salt, as the example As mineral salt, for example, LiClO4, LiPF6, and LiBF4, LiAsF6, LiSbF6, LiI, LiBr, LiCl, LiAlCl, LiHF2, LiSCN, and LiBph4 It is mentioned. etc. -- as organic salt LiCF3 SO3, LiN (CF3 SO2)2, LiN (CF3 CF2 SO2)2, LiN (CF3 SO2) (C4 F9 SO2), and LiC(CF3 SO2) 3 etc. -- fluorine-containing organic lithium salt is mentioned. [for example,] the inside of these, LiPF6 and LiBF4, LiN (CF3 SO2)2, and LiN (CF3 CF2 SO2)2 etc. -- it is desirable. In addition, two or more kinds may be mixed and these solutes may be used.

[0019] Moreover, 0.5-2 mols /of concentration of the solute in the electrolytic solution are [l.] usually 0.5-1.5 mols/l. preferably. In the range which exceeds l. in less than 0.5 mols [l.] /or two mols /, since the conductivity of the electrolytic solution falls, it is not desirable.

[0020] The carbonaceous ingredient as a negative-electrode ingredient which constitutes a cell which can emit [occlusion and] lithiums, such as a pyrolysis object of the organic substance in various pyrolysis conditions, and an artificial graphite, a natural graphite, can be used. Two or more kinds may be mixed and these negative-electrode ingredients may be used. The configuration of a negative electrode has the usable pellet electrode which performed the sheet electrode and press forming which were applied to the charge collector, after mixing with a binder and an electric conduction agent if needed. The quality of the material of the charge collector for negative electrodes has the point of metals, such as copper, nickel, and stainless steel, being used and being easy to process it into a thin film in these, and the point of cost to desirable copper foil.

[0021] As a positive-electrode ingredient which constitutes a cell, the ingredient which can emit [occlusion and] lithiums, such as lithium transition-metals multiple oxide ingredients, such as lithium cobalt oxide and a lithium nickel oxide, is usable. The configuration of a positive electrode has the usable pellet electrode which performed the sheet electrode and press forming which were applied to the charge collector, after mixing with a binder and an electric conduction agent if needed. As for the quality of the material of the charge collector for positive electrodes, metals, such as aluminum, titanium, and a tantalum, or the alloy of those is used. In these, since especially aluminum or its alloy is lightweight, it is desirable in respect of energy density.

[0022] The configuration of a cell has the usable coin type which carried out the laminating of the cylinder type, pellet electrode, and separator of the inside-out configuration which combined the cylinder type, pellet electrode, and separator which made the

sheet electrode and the separator the shape of a spiral. As a separator which constitutes a cell, a porous sheet or a nonwoven fabric etc. which uses polyolefines, such as polyethylene and polypropylene, as a raw material is usable.
[0023]
[Example] Although an example and the example of a comparison are given to below and this invention is explained to it still more concretely, this invention is not limited to these examples, unless the summary is exceeded.
[0024] (Example 1) The carbon black 6 weight section and the polyvinylidene fluoride KF-1000(KUREHA chemistry company make, trade name) 9 weight section were added to the LiCoO2 85 weight section as positive active material, and it mixed, and distributed by the N-methyl-2-pyrrolidone, and what was made into the shape of a slurry was applied to homogeneity on aluminium foil with a thickness of 20 micrometers which is a positive-electrode charge collector, and after desiccation, it pierced in the predetermined configuration and considered as the positive electrode. What mixed the polyvinylidene fluoride 6 weight section same as the above in the artificial-graphite powder KS-44 (TIMCAL, LTD. make, trade name) 94 weight section, was made to distribute by the N-methyl-2-pyrrolidone, and was made into the shape of a slurry as a negative-electrode active material was applied to homogeneity on copper foil with a thickness of 18 micrometers which is a negative-electrode charge collector, and after desiccation, it pierced in the predetermined configuration and considered as the negative electrode. About the electrolytic solution, the phenylethylene carbonate whose phi is a phenyl group in a formula (I) and whose R is hydrogen is dissolved in the mixture (50:50 volume %) of ethylene carbonate and diethyl carbonate at 10% of the weight of a rate, using as a solute the 6 phosphorus-fluoride acid lithium (LiPF6) which fully dried under the desiccation argon ambient atmosphere, and it is LiPF6 further. It dissolved and prepared at a rate of one mol/l. The coin mold nonaqueous electolyte cell as shown in drawing 1 was produced under the desiccation argon ambient atmosphere using these positive electrodes, a negative electrode, and the electrolytic solution. Hereafter, when explained based on drawing 1 , the positive electrode 1 and the negative electrode 2 were held in the positive-electrode can 3 and the obturation plate 4 made from stainless steel, respectively, and the laminating was carried out through the separator 5 into which the electrolytic solution was infiltrated. Then, caulking seal of the positive-electrode can 3 and the obturation plate 4 was carried out through the gasket 6, and the coin mold cell was produced.
[0025] (Example 1 of a comparison) To the mixture (50:50 volume %) of ethylene carbonate and diethyl carbonate, it is LiPF6. The coin mold cell was produced like the example 1 except having used the electrolytic solution which dissolved at a rate of one mol/l.
(Example 2) Phenylethylene carbonate is dissolved in propylene carbonate at 10% of the weight of a rate, and it is LiPF6 further. The coin cell was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.
[0026] (Example 2 of a comparison) It is LiPF6 to propylene carbonate. The coin mold cell was produced like the example 1 except having used the electrolytic solution which dissolved at a rate of one mol/l.
(Example 3) In the example 1, the coin mold cell was produced like the example 1 except having used the diphenyl vinylene carbonate whose phi is a phenyl group in a formula (II) instead of phenylethylene carbonate and whose R is a phenyl group.
[0027] (Example 4) In the example 2, the coin mold cell was produced like the example 2 except having used diphenyl vinylene carbonate instead of phenylethylene carbonate.
[0028] In 25 degrees C, charge termination electrical-potential-difference 4.2V were performed by 0.5mA constant current, and the charge and discharge test was performed for the cell of these examples 1-4 and the examples 1 and 2 of a comparison by discharge-final-voltage 2.5V. The capacity maintenance factor (%) as the discharge capacity per negative-electrode weight of 10 cycle eye in each cell and a 100 cycle eye and a standard of a cycle property is shown in Table 1. It is referred to as capacity maintenance-factor (%) =(100 cycle eye discharge capacity / 10 cycle eye discharge capacity) x100. It is clear from Table 1 that the capacity maintenance factor of direction at the time of using the electrolytic solution containing the annular carbonate which has a phenyl group improves, and a cycle property is excellent. Moreover, in the case of the electrolytic solution of the propylene carbonate independent solvent of the example 2 of a comparison, on the carbon material front face of a negative electrode, propylene carbonate decomposes violently and does not operate as a cell, but when the annular carbonate which has a phenyl group in propylene carbonate contains, actuation becomes possible and discharge capacity and a cycle property are improved remarkably.
[0029]
[Table 1]

表1

	10サイクル目容量（mAh／g）	100 サイクル目容量（mAh／g）	容量維持率（%）
実施例1	270．0	249．2	92．3
実施例2	261．7	230．4	88．0
実施例3	262．4	235．4	89．7
実施例4	249．2	202．3	81．2
比較例1	254．6	223．6	87．8
比較例2	—	—	—

[0030]
[Effect of the Invention] While the protective coating of remarkable stable ionic permeability generates, suppressing disassembly of the electrolytic solution to the minimum and obtaining a high capacity on an electrode by using the organic system solvent which contains the annular carbonate which has a phenyl group in the nonaqueous electolyte rechargeable battery equipped with the negative electrode containing a carbonaceous ingredient, the cell which was excellent in the cycle property can be produced, and it can contribute to the miniaturization of a nonaqueous electolyte rechargeable battery, and high performance-ization.

[Translation done.]